

Dissertationes Forestales 60

Phosphorus retention in forest soils and the functioning of
buffer zones used in forestry

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Academic dissertation

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Phosphorus (P) retention properties of soils typical for boreal forest, i.e. podzolic soil and peat soils, vary significantly, but the range of this variation has not been sufficiently documented. To assess the usefulness of buffer zones used in forestry in removing P from the discharge by chemical sorption in soil, and to estimate the risk of P leaching after forestry operations, more data is needed on soil P retention properties.

P retention properties of soils were studied at clear-cut areas, unharvested buffer zones adjoining the clear-cut and at peatland buffer zone areas. Desorption-sorption isotherms were determined for the humus layer, the mineral soil horizons E, B and C of the Podzol profile and for the surface layer peat (0-15 cm) and the subsurface layer peat (15-30 cm). The efficiency of buffer zones in retaining P was studied at six peatland buffer zone areas by adding P-containing solute in the inflow. A tracer study was conducted at one of the buffer zone areas to determine the allocation of the added P in soil and vegetation.

Measured sorption or desorption rather than parameter values of fitted sorption equations described P desorption and sorption behaviour in soil. The highest P retention efficiency was in the B horizon and consequently, if contact occurred or was established between the soluble P in the water and the soil B horizon, the risk of P leaching was low. Humus layer was completely incapable of retaining P after clear-cutting. In the buffer zones, the decrease in P retention properties in the humus layer and the low amount of P sorbed by it indicated that the importance of the layer in the functioning of buffer zones is low.

The peatland buffer zone areas were efficient in retaining soluble P from inflow. P sorption properties of the peat soil at the buffer zone areas varied largely but the contribution of P sorption in the peat was particularly important during high flow in spring, when the vegetation was not fully developed. Factors contributing to efficient P retention were large buffer size and low hydrological load whereas high hydrological load combined with the formation of preferential flow paths, especially during early spring or late autumn was disadvantageous. However, small buffer zone areas, too, may be efficient in reducing P load.

Keywords: humus layer, isotherm, peat, $\text{PO}_4\text{-P}$, Podzol, sorption

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LIST OF ORIGINAL ARTICLES

This thesis consists of the summary and the following substudies, which are referred to in the text by their Roman numerals.

- I Väänänen, R., Hristov, J., Tanskanen, N., Hartikainen, H., Nieminen, M. & Ilvesniemi, H. Phosphorus sorption properties in podzolic forest soils and soil solution phosphorus concentrations in undisturbed and disturbed soil profiles. In press.
- II Väänänen, R., Kenttämies, K., Nieminen, M. & Ilvesniemi, H. 2007. Phosphorus retention properties of forest humus layer in buffer zones and clear-cut areas in southern Finland. *Boreal Environment Research* 12: 601-609.
- III Väänänen, R., Nieminen, M., Vuollekoski, M., Nousiainen, H., Sallantausta, T., Tuittila, E.-S. & Ilvesniemi, H. 2008. Retention of phosphorus by peatland buffer zones at six forested catchments in southern Finland. *Silva Fennica* 42: 211-231.
- IV Väänänen, R., Nieminen, M., Vuollekoski, M. & Ilvesniemi, H. 2006. Retention of phosphorus in soil and vegetation of a buffer zone area during snowmelt peak flow in southern Finland. *Water, Air and Soil Pollution* 177: 103-118.

In Paper I Riitta Väänänen was responsible for conducting the data analysis and was the main author in the manuscript. In Papers II, III and IV Väänänen participated in planning the research, was mainly responsible for conducting field experiments, laboratory work and data analysis, and was the main author in the manuscripts.

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1. INTRODUCTION

1.1. The load of phosphorus in Finland

Phosphorus (P), along with nitrogen (N), is the growth limiting nutrient in most boreal lake ecosystems and in the Baltic Sea (Pietiläinen and Räsänen 1999 and the references within). The input of these nutrients into watercourses has increased by human activity. Today, the annual leaching of P from terrestrial systems in Finland is approximately 6800 tons of which 2700 tons is estimated to be naturally occurring background leaching. Of the 4100 tons of anthropogenic load approximately 13% originates from point sources and 80% leaches as diffuse load. Most of the diffuse load originates from agricultural land, scattered settlement without municipal water supply and sewerage and from operated forestry areas (Finnish Environment Institute, unpublished data) (Fig. 1).

During the past decades, the proportion between point source and diffuse load had dramatically changed, since still in the 1970's, P load from point load sources exceeded diffuse load (Kauppi 1979). Decrease in point source load has even continued in 1995–2005 (Fig. 1), but no clear signs of decrease can be seen in the diffuse load (Räsänen et al. 2003). Therefore, the major contemporary challenge in reducing eutrophication of surface waters is the control of nutrient leaching from anthropogenic diffuse load sources.

Even though agriculture causes the largest diffuse P load in Finland on national scale, the environmental impact of forestry can locally be large because forestry is also practiced in areas where other anthropogenic actions are insignificant. In 1998, a Decision-in-Principle was issued on the water protection targets, which called for a decrease in anthropogenic P load by about 45% from the levels in 1991–1995 (Vesiensuojelun tavoitteet vuoteen... 1998). Forestry organizations responded to this demand by adding water protection practices, such as the

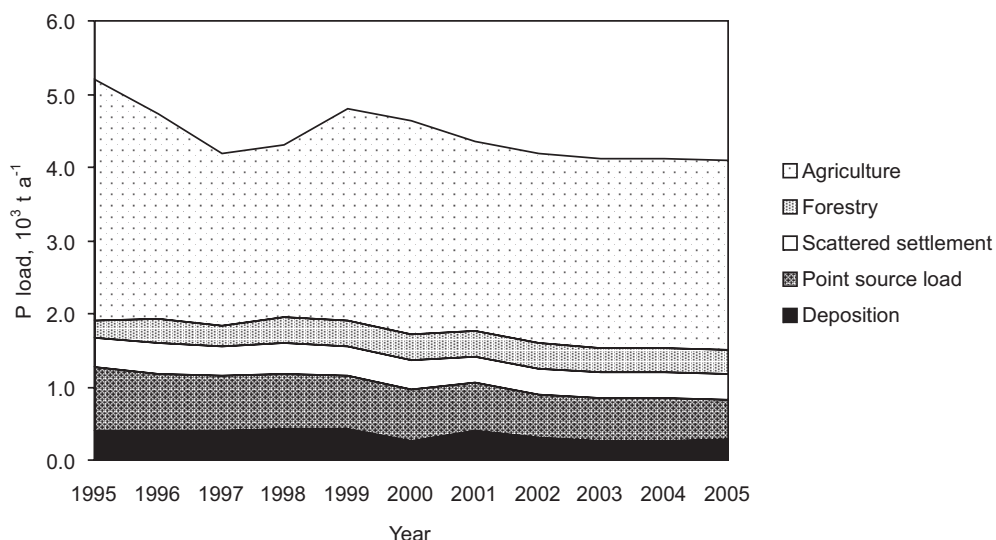


Figure 1. Annual anthropogenic P load from diffuse load sources (agriculture, forestry and scattered settlement without municipal water supply and sewerage), point sources and from deposition (Finnish Environment Institute, unpublished data)

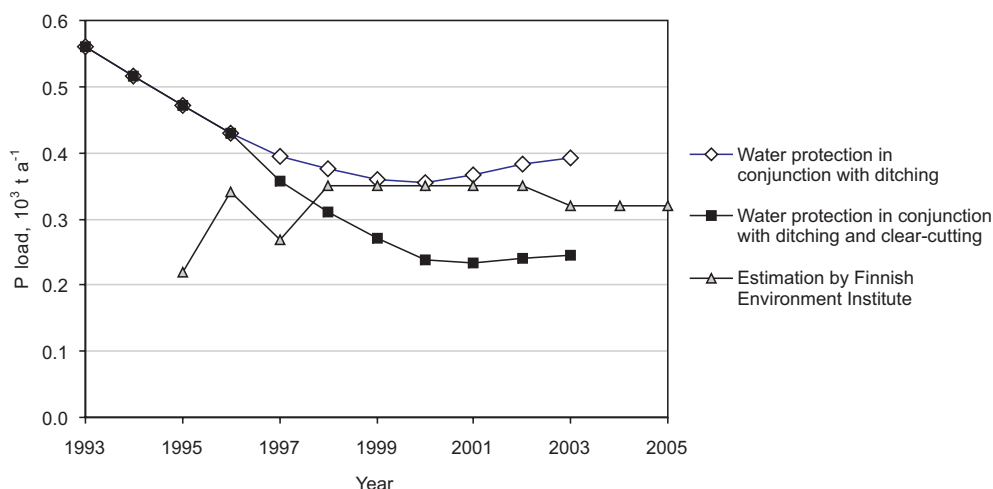


Figure 2. Two estimates of anthropogenic P leaching from forestry land in Finland: leaching in 1993–2003 by Leivonen (2005) and in 1995–2005 by the Finnish Environment Institute (unpublished data).

use of buffer zones to reduce sediment and soluble nutrient load from forestry areas, to the recommended methods of good forestry practices (Metsätalouden ympäristöopas 1997). According to an evaluation report the total P load from forested area has decreased from 561 to 245–392 tons during 1993–2003, which equals to a 30% – 56% reduction (Leivonen 2005). Another estimate by the Finnish Environment Institute shows no reduction in 1995–2005 (Fig. 2). The estimate in the evaluation report (Leivonen 2005) is based on implemented forestry operations and assumes that water protection practices have been applied in conjunction with ditching, or with both ditching and harvesting, and that these practices have been successful in reducing P. The assumption of successful P retention by buffer zones may, however, be optimistic because several studies indicate that the effect of buffer zones can be negligible or, in the worst case, they can even increase P transport (see e.g. Sallantausta et al. 1998, Liljaniemi et al. 2003, Nieminen et al. 2005b). Further research is needed to provide reliable estimates on the actual P retention efficiency of buffer zone areas currently used in forestry.

1.2. The effect of forestry operations on P leaching

Leaching of P from forestry land in Finland is approximately 2–18 kg km⁻² annually (Rekolainen 1989, Kenttämies 1998, Kortelainen and Saukkonen 1998, Vuorenmaa et al. 2002). Of this amount approximately half is background leaching (Mattsson et al. 2003) and the rest has been induced by forestry operations (Kauppi 1979, Rekolainen 1989, Kortelainen and Saukkonen 1998, Vuorenmaa et al. 2002). This leaching of total P contains both soluble phosphate (PO₄-P), dissolved organic P and particulate P, i.e. P bound in inorganic or organic solids. In the ecological sense the most significant difference between these P forms is that PO₄-P is almost completely available for algal assimilation whereas particulate P is mostly not (Ekholm 1998) and therefore less significant in eutrophication of water ecosystems. The proportion of soluble and solid forms of P of the total P load varies depending on the catchment type and forestry operation performed

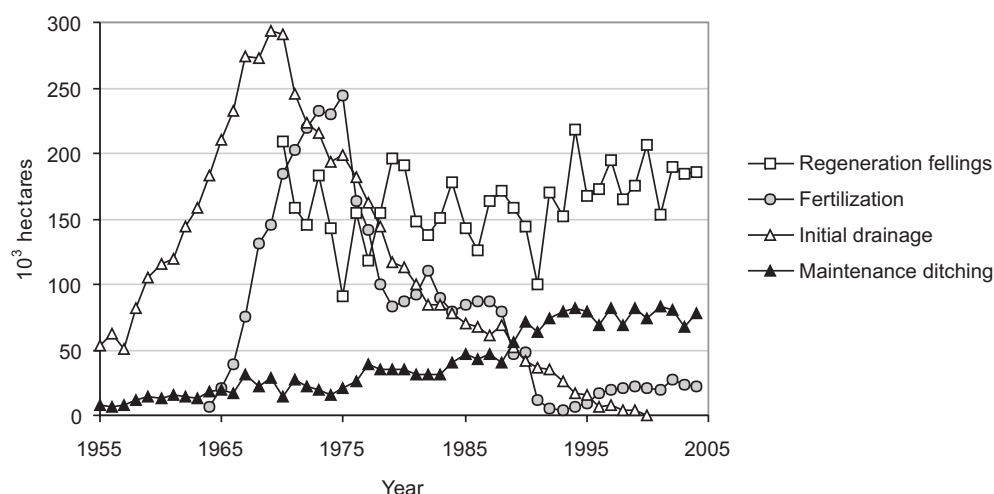


Figure 3. Areas of initial drainage and maintenance ditching from 1955, fertilization from 1964 and regeneration fellings from 1970 to 2004 (Statistical Yearbook of... 1995, Finnish Statistical Yearbook... 2005).

in the catchment. In unmanaged catchments, the proportion of $\text{PO}_4\text{-P}$ is 25% – 60% of the total P (Kenttämies 1981, Ahtiainen and Huttunen 1999, Mattsson et al. 2003). Forest ditching causes increase in solid load and thus it usually increases the transportation of P bound in solids more distinctively than $\text{PO}_4\text{-P}$ (Manninen 1998) whereas fertilizer application especially increases the proportion of $\text{PO}_4\text{-P}$ in the water discharge (Kenttämies 1981).

Regeneration fellings are the most extensive forest management operation when measured with area operated each year (Fig. 3) and over 80% of regeneration fellings are implemented as clear-cutting (Finnish Statistical Yearbook of Forestry 2005). The effect of clear-cutting on the outflow of P has been followed in several catchment level studies (e.g. Knighton and Stiegler 1980, Stevens et al. 1995, Ahtiainen and Huttunen 1999, Lundin 1998, 1999, Cummins and Farrell 2003, Neal et al. 2003, Nieminen 2003, 2004). Clear-cuttings increase the concentrations of total P and $\text{PO}_4\text{-P}$ in stream water especially when the operation is performed on peatland forests (Knighton and Stiegler 1980, Ahtiainen and Huttunen 1999, Lundin 1999, Cummins and Farrell 2003, Nieminen 2003). The highest increase in P load generally occurs in the first two years following harvesting (Ahtiainen and Huttunen 1999). In future, there is a growing need to increase the proportion of harvesting on peatland forests (Finland's National Forest... 1999), i.e. in forest areas where the leaching risk of P is largest.

The increase in P load after clear-cutting results from an increase in the labile P pool in the harvested area. The removal of trees suppresses plant P uptake and P released to soluble form from decomposing logging residues and as a result of the increased mineralization of the organic soil layer further increases the labile P pool in the surface soil layer (Bekunda et al. 1990, Stevens et al. 1995, Hyvönen et al. 2000, Neal et al. 2003, Palviainen et al. 2004, Piirainen et al. 2004). In addition, soil surface is often disturbed by the harvesting and stem transporting machinery if harvesting takes place during snow free period, and especially when the soil is prepared for forest regeneration by ploughing, scarifying, ditching or mounding. These procedures increase the risk of leaching of suspended solids and consequently leaching of particulate P to recipient waters (Ahtiainen and Huttunen 1999, Nieminen 2003).

In Finland, approximately 4.9 million hectares of peatland and 1.3 million hectares of waterlogged mineral soils in the upland have been drained for forestry (Finnish Statistical Yearbook... 2005). The annually drained peatland area was at the highest in 1969, when approximately 294 000 hectares were ditched, after which initial drainage of pristine peatlands rapidly decreased and completely ceased by 2000 (Statistical yearbook of... 1995, Finnish Statistical Yearbook... 2005) (Fig. 3). Today, instead of initial drainage there is a growing need for maintenance ditching operations, i.e. ditch cleaning and supplementary ditching of the forest or peatland areas initially drained several decades ago. In 2004, maintenance ditching was performed on 78 000 hectares of drained peatlands and the target is to increase the area to 110 000 hectares per year (Finnish Statistical Yearbook... 2005, Finland's National Forest... 1999).

A distinct effect of initial ditching is the increase in sediment load in the recipient waters (Kenttämies 1981, Seuna 1982, Ahtiainen and Huttunen 1999) and the effects of maintenance ditching are similar (e.g. Manninen 1998, Joensuu et al. 1999, Åström et al. 2001a, 2001b, Joensuu et al. 2002, Åström et al. 2005). However, the loading effect of initial ditching is typically higher because it intensifies drainage more than maintenance ditching. Increased sediment transport typically peaks during the excavation, remains high during the following year and continues at elevated level 5–10 years after the operation. Particularly high sediment leaching occurs if the ditches extend to a mineral soil layer beneath the peat soil (Seuna 1982, Ahtiainen and Huttunen 1999, Åström et al. 2001a). Ditching and maintenance ditching can also increase leaching of soluble and particulate P (Manninen 1998, Ahtiainen and Huttunen 1999, Åström et al. 2005). The loading effect for total P peaked during the first five years after the operation whereas $\text{PO}_4\text{-P}$ loading continued up to ten years (Ahtiainen and Huttunen 1999). However, other studies indicate that the effect of forest drainage on P outflow can be insignificant if the transport of P bound in sediment, i.e. particulate P, can be prevented (Joensuu et al. 2002) and the hydrogeochemistry of iron (Fe) in the catchment area remains unchanged (Åström et al. 2002).

The application history of P fertilization has had the largest effect on the variation in P runoff from forested catchments (Kortelainen and Saukkonen 1998). Fertilizer P along with potassium (K) has been applied to peatland forests to increase their productivity whereas nitrogen is considered to be the growth limiting nutrient in upland forests. The application of forest fertilizers increased steadily until 1975, when a total of 244 000 hectares were fertilized, after which forest fertilization decreased and reached the lowest point in 1993 (4 000 hectares) and since then, has increased to 22 000 hectares by 2004 (Statistical yearbook of... 1995, Finnish statistical yearbook... 2005) (Fig. 3).

Fertilizer-induced P leaching is particularly high when the P-fertilizer contains water soluble P and is spread during winter on snow (Nieminen and Ahti 1993). Leaching is typically highest in the first and second year after fertilization and P concentrations in the outflow water may remain at a higher level than before fertilizing for several years, even over a decade (Kenttämies 1981, Ahti 1983, Malcolm and Cuttle 1983, Nieminen and Ahti 1993, Miller et al. 1996, Ahtiainen and Huttunen 1999, Joensuu et al. 2001). The increase in P load after forest fertilizing is approximately $20\text{--}200 \text{ kg km}^{-2} \text{ a}^{-1}$ and the load can be $6\text{--}9 \text{ kg km}^{-2} \text{ a}^{-1}$ higher than the background leaching over ten years after fertilizer application (Särkkä 1970, Kauppi 1979, Ahti 1983, Nieminen and Ahti 1993, Joensuu et al. 2001). Thus, forest fertilizing increases P leaching for a longer period of time than clear-cutting or drainage. The long-lasting loading effect of P fertilization may result from the low dissolution rate of P fertilizers typically used in forestry as well as low P retention capacity of peat soils (Nieminen and Jarva 1996).

1.3. P retention in forest soils

In acid soils, which are typical for the forests of Finland, the most important components in P chemical retention are aluminium (Al) and iron (Fe) oxides and hydroxides (e.g. Hartikainen 1979, Peltovuori 2006) by which soluble P is retained by a ligand exchange mechanism (Hingston et al. 1967). The term sorption is suggested to be used in stead of adsorption for chemical P retention to cover the various phases of P binding to oxides (Peltovuori 2006).

P sorption in soil is often studied as an equilibrium reaction where the amount of sorbed P is described as a function of P concentration in solution. Empirical analysis of this response results in a set of measurements which graphically plotted form a curve, which is called desorption-sorption isotherm. An equation can then be fitted to the measurements to achieve a numerical description of the retention phenomenon. The Langmuir equation has widely been used to describe desorption-sorption in soil, probably because it produces a parameter value which is considered to describe the theoretical maximum P retention (e.g. Barrow 1978). The initial mass isotherm presents sorption as a function of the change in the initially added P and the slope of the linear curve describes retention efficiency (Nodvin et al. 1986). In addition, several single point sorption indices to describe P retention have been developed (Bache and Williams 1971, Simard et al. 1994).

The interest in developing these methods originates from a need to understand the ability of agricultural soils to maintain the level of P in soil solution suitable for crop growth. Therefore, careful assessment is needed when applying these methods to describe P retention properties in forest soils. The use of Langmuir equation and single point sorption index have been applied to peat soils in Finland (Heikkinen et al. 1995, Nieminen and Jarva 1996) and the results suggest that the value for the retention maximum overestimates the actual retention ability of peat. Therefore, applicability of different methods in describing and quantifying P sorption in a wider range of forest soils needs to be evaluated.

The upland soils in Finland are mostly podzolic (FAO – Unesco 1981). At national scale, P retention properties of podzolic soils have been less studied but it is generally acknowledged that the illuvial B horizon of a podzolized soil profile is efficient in sorbing P due to the enrichment of Al and Fe compounds in the horizon (e.g. Burnham and Lopez-Hernandez 1982, Wood et al. 1984, Borggaard et al. 1990, Yuan and Lavkulich 1994, Li et al. 1999). P retention in the eluvial E horizon, where Al and Fe have been depleted, has received less attention but apparently retention is significantly lower than in B horizon (Burnham and Lopez-Hernandez 1982, He et al. 1998, Nair et al. 1998). P retention properties of the organic humus layer overlying the mineral soil are poorly documented. The amounts of Al and Fe are generally low in the humus layer (Tamminen and Starr 1990, Westman 1990, Tyler 2004), which implies a low P retention, but enrichment of these compounds and consequently high P retention efficiency has also been reported (Giesler et al. 2002).

Approximately 34% (9.1 million hectares) of the forestry land in Finland is classified as peatlands (Finnish Statistical Yearbook... 2005). Previous studies have shown that some peat soils are completely incapable of retaining P while others show P retention which is typically lower than in mineral soils enriched with Al and Fe (Kaila 1959, Heikkinen et al. 1995, Nieminen and Jarva 1996). The rate of forest clear-cuttings, ditch cleaning and supplementary drainage on drained peatlands in Finland may undergo a rapid increase in the near future, and because of their low phosphorus sorption capacity, there is a growing need for water protection methods that reduce P transport to downstream water bodies.

Podzolic upland soils and peatlands, i.e. typical soils in managed forest areas vary largely in their P retention properties. The range of this variation and its effect on the P leaching or

retention potential by the managed forest area is difficult to evaluate because the data on P retention properties of Finnish forest soils is limited. In addition, the variation in the study methods used in the previous studies limits the comparability of the current data. The data is particularly needed to evaluate P retention or release by forest soils under elevated P load, such as after harvesting, and to evaluate the functioning potential of buffer zones. The increased P load to soil from harvested and drained forest areas continues for several years. However, little information is available on the response of forest soils to long-term P loading.

1.4. P retention by buffer zone areas

To prevent P leaching from managed forest land, it is recommended to combine water protection practices with forestry operations (Metsätalouden ympäristöopas 2004, Hyvän metsänhoidon suositukset 2006). One of the recommended practices is to excavate sedimentation ponds in maintenance ditching and peat mining areas (e.g. Joensuu 2002, Ihme 1994). Sedimentation ponds typically reduce part of the sediment load, particularly heavy and coarse fractions, but they are inefficient in reducing soluble nutrients from water flow, and completely fail in removing soluble P (Joensuu 2002, Ihme et al. 1991).

Today, the use of buffer zone areas is recommended in conjunction with forestry operations such as harvesting and maintenance ditching (Metsätalouden ympäristöopas 2004, Hyvän metsänhoidon suositukset 2006). The aim of these buffer zones is to create areas where physical, biological and chemical processes reduce particulate and soluble nutrient load from the runoff before it enters in a watercourse. The processes removing P include sedimentation of particulate P, assimilation of soluble P by the biota and chemical retention of soluble P by sorption in soil or by precipitation and deposition (e.g. Richardson and Marshall 1986, Cooke 1992, Uusi-Kämppe et al. 2000, Liikanen et al. 2004). When a forest area is harvested, buffer zones are typically left along watercourses. Depending on the water protection requirements, the width and the management of these riparian buffer zone areas varies, i.e. they may be either cautiously harvested or left completely unmanaged (Metsätalouden ympäristöopas 2004, Hyvän metsänhoidon suositukset 2006). Water protection practices recommended when forest area is drained are the use of sedimentation ponds and directing the outflow water over a buffer zone area, which is typically peatland, before entering an open watercourse (Metsätalouden ympäristöopas 2004, Hyvän metsänhoidon suositukset 2006).

Removal of particulate P as well as other suspended solids requires that the transportation capacity of the water flow is reduced by the buffer zone. This reduction is typically achieved by redirecting the water flow to spread it over a relatively flat area where sheet flow or subsurface flow prevails instead of channel flow. Several studies have indicated that buffer zone areas are efficient in reducing suspended solids (Ihme 1994, Sallantausta et al. 1998, Ahtiainen and Huttunen 1999, Kubin et al. 2000, Lacey 2000, Nieminen et al. 2005a). Large buffer zones retain more suspended solids than small ones indicating that sufficiently large surface area is a critical factor for efficient sediment removal by the buffer zone areas (Nieminen et al. 2005a).

The mechanisms proposed to remove soluble P and other soluble compounds from inflow are complex and the success of buffer zones in retaining $\text{PO}_4\text{-P}$ from runoff is more ambiguous. A complete removal of P by buffer zone has rarely been reported (Ahtiainen and Huttunen 1999, Kubin et al. 2000) and in some cases the use of buffer zone areas has even resulted in a considerable increase in P leaching (Liljaniemi et al., 2003, Sallantausta et al. 1998, Vasander et al. 2003). However, several studies report that typically peatland buffer zones act as sinks of P

but, temporarily, the outflow concentration of P can exceed P in inflow (Ihme 1994, Sallantausta et al. 1998, Nieminen et al. 2005b, Silvan et al. 2005). The varying success of previously studied buffer zone areas in reducing soluble P load raises the question whether buffer zones recommended in good forestry practise are functional at all. With the current level of understanding definite conclusions of their efficiency cannot be drawn and therefore, the possibilities of buffer zone areas in retaining P still need further evaluation. The varying conditions of the buffer zone areas studied so far, such as size, vegetation composition, soil type, management history, life and construction method, environmental conditions during the study period, and the length of the study complicates the detection of the common nominators for their P retention performance. In order to find the factors which have the largest impact of P retention efficiency in buffer zones, an experimental design with several replications of the same treatment could provide data suitable for generalization of the results.

In most studies the P retention efficiency of the buffer zone area has been evaluated from the differences in P concentration between inflow and outflow water (e.g. Sallantausta et al. 1998, Liljaniemi et al. 2003, Nieminen et al. 2005b) or differences in stream water concentrations between areas with and without a buffer zone (Ahtiainen and Huttunen 1999). These studies provide little information on the actual processes controlling P retention or release. The connection between P reduction by buffer zones and P assimilation by biota has received attention in previous studies (Richardson and Marshall 1986, Kellogg and Bridgham 2003, Silvan et al. 2003). These studies have shown that in peat soil microbes are important in assimilating additional P and they form an initial fast P retaining sink; however, their P retention capacity can saturate if the elevated load continues (Richardson and Marshall 1986, Kellogg and Bridgham 2003, Silvan et al. 2003). P retention by vegetation, especially by sedges in peatlands in Finland, follows the initial fast microbial assimilation and forms an important P sink over a growing period (Richardson and Marshall 1986, Kellogg and Bridgham 2003, Silvan et al. 2004a, 2004b). However, a large part of assimilated P is released after the growing period when biomass is decomposed (Richardson and Marshall 1986) and a long-time effect of vegetation in binding excess P can be negligible (Huttunen et al. 1996). In addition, approximately 50% of the annual P load leaches during the snowmelt period early in spring before the start of the growing period (Kortelainen and Saukkonen 1998) when the annual vegetation cover has not yet developed and therefore may have a limited potential in removing P. The significance of soil and vegetation in binding P in these conditions still needs to be examined.

1.5. Aims of the study

The aim of this study was to describe P retention properties of Finnish forest soils with the specific attempt to relate soil P retention properties to the functioning of buffer zone areas used in forestry and to the risk of increased P runoff following forestry operations.

Specific aims were

- to produce uniform data on the P retention properties of typical soils in Finnish forests (I, II, III, IV)
- to identify the role of soil P retention capacity on the functioning of buffer zone areas (II, III, IV)
- to determine the P retention efficiency of peatland buffer zone areas used in forestry and the factors influencing on the efficiency (III, IV)
- to quantify the allocation of retained P in soil and vegetation in a peatland buffer zone area (IV)
- to assess the changes in soil P retention capacity as a result of long-term P load (II, III).

2. MATERIAL AND METHODS

2.1. Research areas, experimental designs and soil sampling

2.1.1. *P* retention in podzolic upland soil

P retention properties of a podzolic upland soil were studied at Haukkakangas site in Ruovesi in southern Finland (Fig. 4, Table 1, Paper I). At the site the trophy formed a gradient from fertile *Oxalis-Maianthemum* type (OMT) to medium fertile *Myrtillus* type (MT) and to less fertile *Vaccinium vitis-idaea* (VT) type upland forest (site type classification after Cajander 1926). The sites had developed on glacio-fluvial sorted material over approximately 10 000 years and the soil at all sites was Haplic Podzol (FAO – Unesco 1990). Five years before the study the forest growing on the site (130 to 140-year-old mixed Norway spruce and Scots pine) had been harvested using conventional stem-only harvesting, where cutting residues were left on the site.

Three soil sampling points were placed along the fertility gradient at each site type at approximately 50 m intervals (Paper I). The samples were collected in 2002 (Table 2). Soil P retention properties were determined for each morphological soil horizons (O, E, B and C) separately.

2.1.2. *P* retention in the humus layer of clear-cut areas and unharvested buffer zones

Three small forested catchments (C1, C2 and C3) were selected to study the P retention in the humus layer in clear-cut areas and in adjacent buffer zones, and the effect of long-term P load on humus P retention (Table 1, Fig. 4, Paper II). The clear-cuttings in these catchments were carried out in 1997 in C1 and 1998 in C2 and C3 using conventional stem-only harvesting. The harvested areas were prepared for planting by scarification and Norway spruce seedlings were planted one (C2 and C3) or two (C1) years after harvesting. At each area, an unharvested buffer zone was left along the main outlet ditch or brook. The width of the buffer zone was 10–35 m at C1, about 10 m at C2, and 20 m at C3.

Humus layer samples were collected from the clear-cut areas and the adjoining unharvested buffer zones (Paper II). For humus in the clear-cut areas, there were two sampling points in C1 and C3 and four in C2. The corresponding number of sampling points for the humus layer in the buffer zones was one for C1 and C3 and two for C2. Volumetric core samples were taken from an undisturbed humus layer. The first samples were collected in the first autumn after harvesting in 1997 in C1 and 1998 in C2 and C3 and the sampling was repeated in 2001 from the same points as in the first sampling (Table 2). P retention properties of the humus layer were determined for the clear-cut areas and the buffer zones and retention properties between sampling locations and times were compared (Paper II).

2.1.3. *P* retention in peatland buffer zone areas

P retention by peatland buffer zones were studied at five areas which received inflow from maintenance ditched watersheds (Asusuo, Kirvessuo, Murtsuo, Kallioneva and Hirsikankaansuo), and at one area, which received inflow from a harvested upland area (Vanneskorvenoja) (Table 1, Fig. 4, Paper III). The peatland buffer zones had been constructed or taken into use in conjunction with the forestry management in the catchment in 1996–1999

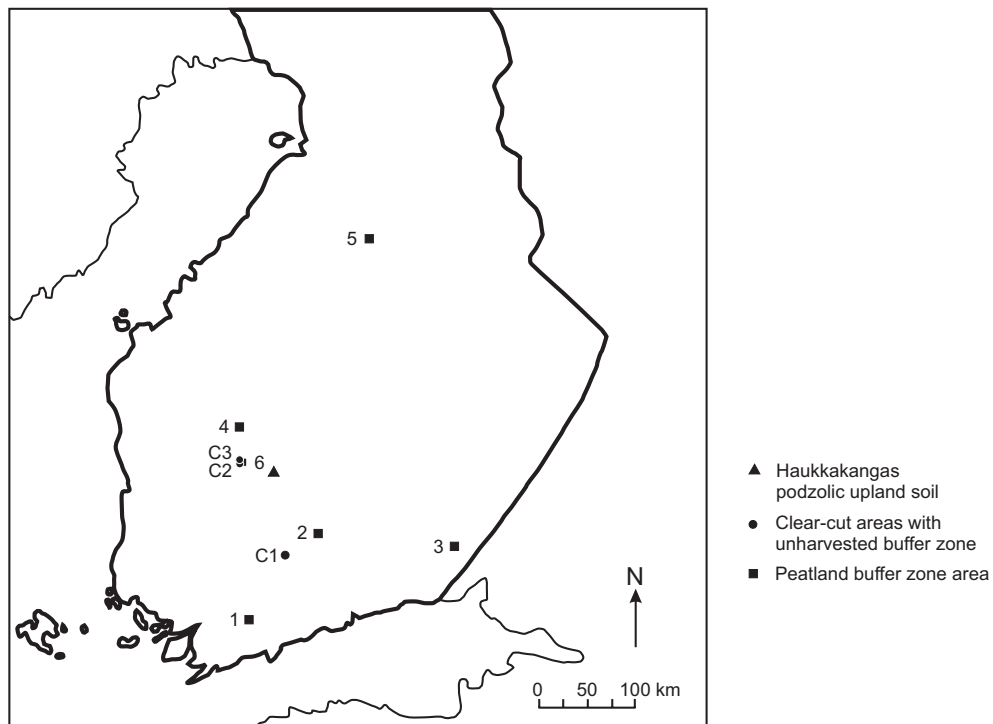


Figure 4. Locations of the research areas. The Haukkakangas podzolic upland soil is located in Ruovesi. Clear-cut area with unharvested buffer zone C1 is in Janakkala and C2 and C3 in Kuru. The peatland buffer zone areas are numbered as follows: 1. Asusuo in Kiikala, 2. Kirvessuo in Asikkala, 3. Murtsuo in Lappeenranta, 4. Kallioneva in Virrat, 5. Hirsikankaansuo in Pyhäntä and 6. Vannesorvenoja in Kuru.

by either restoring and rewetting a section of the drainage area or by directing the outflow water from the drainage area to an undrained peatland area downstream (Table 1). The sizes of the buffer zones varied from 0.12 to 1.03 hectares, accounting for 0.1% – 4.9% of the area of the watershed. Most of the water flow at the buffer zones occurred as overland flow (channel flow or sheet flow) across the relatively flat areas. Channel flow was considerable at the Asusuo, Kirvessuo, Murtsuo and Hirsikankaansuo buffer zones, while almost no channel flow occurred at the Kallioneva buffer zone. At all buffer zones, the average depth of the peat layer was over 1 meter. In the Asusuo buffer, the peat profile also contained mineral soil layers of varying thickness. The probable explanation of these mineral soil layers was that they were formed of the soil material that was eroded from the ditches of the peatlands upstream during and after their initial drainage in 1967.

A phosphate phosphorus ($\text{PO}_4\text{-P}$) solution was added to the inflow water of each of the buffer zone areas (Paper III). Each buffer zone received a total of 10 kg of $\text{PO}_4\text{-P}$. At Asusuo, Kirvessuo, Murtsuo and Kallioneva the addition was given during five consecutive days in 2003 (Table 2). Hirsikankaansuo and Vannesorvenoja received the $\text{PO}_4\text{-P}$ addition at two four-day periods: 3 kg in 2004 and 7 kg in 2005. During each adding period, KH_2PO_4 was daily dissolved in the local runoff water in a container which released the solution at an approximately constant rate into the runoff water (Fig. 5).

Table 1. Study areas, their location, mean summer and winter temperature, precipitation, area and site description.

	Location	Mean temperature ¹ January June	Precipitation ² Total Snow	Area, ha	Area, % of watershed area	Site description	Site type ³
<i>Podzolic upland soils</i>							
Haukkakangas	61°50'N 24°22'E	-7.8°C 15.5°C	710 mm 200 mm	Upland	<i>Oxalis Maianthemum</i> type, <i>Myrtillus</i> type, <i>Vaccinium vitis-idaea</i> type
C1	61°00'N 24°43'E	-6.1°C 16.4°C	650 mm 200 mm	0.20	2.8	Upland	<i>Myrtillus</i> type
C2	61°52'N 23°41'E	-7.3°C 15.5°C	680 mm 250 mm	0.16	3.1	Upland	<i>Myrtillus</i> type, <i>Vaccinium vitis-idaea</i> type
C3	61°52'N 23°41'E	-7.3°C 15.5°C	680 mm 250 mm	0.46	6.3	Upland	<i>Myrtillus</i> type, <i>Vaccinium vitis-idaea</i> type
<i>Clear-cut areas with unharvested buffer zones</i>							
<i>Peatland buffer zone areas</i>							
Asusuo	60°26'N 23°37'E	-5.6°C 16.7°C	710 mm 250 mm	0.16	0.23	Pristine mire	Tall-sedge spruce swamp
Kirvessuo	61°14'N 25°16'E	-7.4°C 13.8°C	680 mm 200 mm	0.12	0.09	Drained peatland forest	Herb-rich type drained peatland forest
Murtsuo	61°01'N 28°19'E	-8.0°C 17.2°C	630 mm 250 mm	0.16	0.16	Drained peatland forest	<i>Myrtillus</i> type drained peatland forest
Kallioneva	62°16'N 23°48'E	-7.8°C 15.5°C	710 mm 200 mm	1.03	4.9	Pristine mire	Tall-sedge fen
Hirsikankaansuo	64°04'N 26°40'E	-9.9°C 15.5°C	630 mm 250 mm	1.01	1.1	Pristine mire	Low-sedge bog
Vanneskorvenoja	61°51'N 23°42'E	-7.3°C 15.5°C	680 mm 250 mm	1.00	2.5	Drained peatland forest	<i>Vaccinium vitis-idaea</i> type, <i>Myrtillus</i> type; herb-rich type drained peatland forests

¹ Climatological statistics of ... 2002.² Atlas of Finland 1987.³ Site types for pristine mires and drained peatlands according to Heikurainen and Pakarinen (1982), for mineral soils according to Cajander (1926).

Table 2. Soil sampling years, inflow and outflow water sampling years for the peatland buffer zone areas, and the years of PO₄-P and ³²P addition experiments for the peatland buffer zone areas.

	Soil samples		Inflow and outflow water sampling	PO ₄ -P adding		³² P adding
	1st sampling	2nd sampling		1st period	2nd period	
Podzolic upland soil						
Haukkakangas	2002	-	-	-	-	-
Clear-cut areas with unharvested buffer zones						
C1	1997	2001	-	-	-	-
C2	1998	2001	-	-	-	-
C3	1998	2001	-	-	-	-
Peatland buffer zone areas						
Asusuo	2001	2003	2003–2006	2003	-	2003
Kirvessuo	2001	2003	2003–2006	2003	-	-
Murtsuo	2001	2003	2003–2006	2003	-	-
Kallioneva	2001	2003	2003–2006	2003	-	-
Hirsikankaansuo	2001	-	2004–2006	2004	2005	-
Vanneskorvenoja	-	-	2005–2006	2005	2006	-

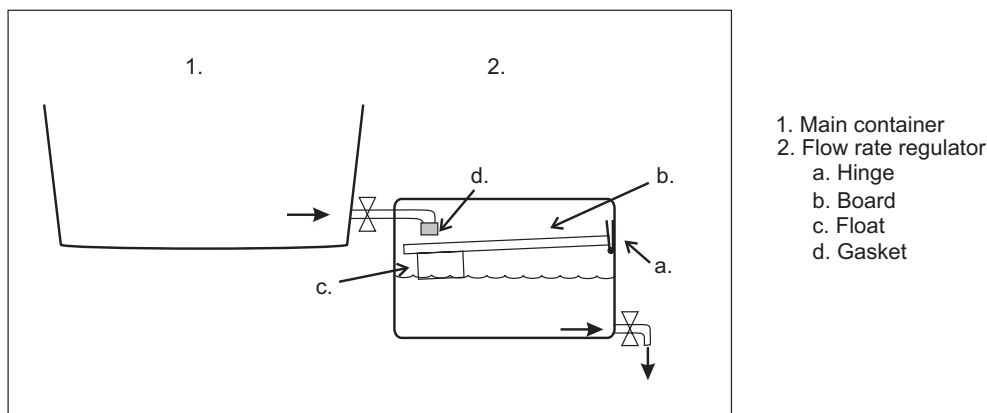


Figure 5. The equipment used in the P adding experiment consists of a 200-liter main container (1) and a secondary, 15-liter container that acts as a flow rate regulator (2). The flow rate from the secondary container can be controlled accurately with a valve because the fluid level in the secondary container is kept constant with a simple regulatory mechanism. When inflow from the main container fills the secondary container, a hinged board (a, b) with a float (c) moves up until the board meets the feeder tube from the main container. The back of the board is pressed against a gasket (d) made of silicone tubing over the main feeder tube. This slows down the flow from the main container to the same level as the outflow from the secondary container.

At each peatland buffer zone area, sampling of the inflow and outflow waters was started on the same day with the $\text{PO}_4\text{-P}$ addition and samples were collected daily throughout the adding period (Table 2). After the adding had ended, follow-up continued for 2–4 years during which 2–18 inflow and outflow samples were taken annually during the snow-free season at each buffer zone area (Paper III, Table 2).

From Asusuo, Kirvessuo, Murtsuo and Vanneskorvenoja the runoff was measured at a V-notch weir during the study period, and from Hirsikankaansuo during the first adding period in 2004 (Paper III). Runoff from Hirsikankaansuo at 2005 and from Kallioneva during the whole study period was estimated using daily runoff data collected at nearby catchments by the Finnish Environment Institute (unpublished data).

To determine the extent of water spreading over the buffer zone areas, surface water samples were taken daily during the adding period from the Asusuo, Kirvessuo, Murtsuo and Kallioneva study areas. The sampling points formed a regular grid covering the buffer zone area and 10–25 samples per buffer zone area were collected seven times: before and during the adding period and 5–8 days after the adding had ended (Paper III). At Hirsikankaansuo during the last P adding day in 2005, an 80-m-long sampling line was laid across the buffer zone and the movement of P was studied from 8 sampling points at 10 m intervals.

To study the allocation of the added $\text{PO}_4\text{-P}$ in the soil and vegetation in the buffer zone area, radiotracer ^{32}P was introduced to Asusuo by mixing it with the $\text{PO}_4\text{-P}$ solution in 2003 (Paper IV, Table 2). A daily addition of 37 MBq of $^{32}\text{PO}_4$ (carrier-free in dilute HCl) was added to the $\text{PO}_4\text{-P}$ solution, thus Asusuo buffer received a total of 185 MBq of $^{32}\text{PO}_4$. The recovery of the added ^{32}P was studied from soil, moss and vascular plant samples taken five days after the adding had ended, i.e. ten days after the start of the adding period. Soil samples were taken as described above for Asusuo. The green parts of the moss samples were harvested from a 1-dm² area at the sampling point and the aboveground parts of the vascular plant samples were cut with scissors from a 4-dm² area.

Peat samples were collected from the peatland buffer zone areas with the exception of Vanneskorvenoja. The first samples were taken in 2001 and sampling was repeated at Asusuo, Murtsuo, Kirvessuo and Kallioneva buffer zone areas in 2003 after the $\text{PO}_4\text{-P}$ addition experiment (Table 2). For soil sampling, 10–26 volumetric soil samples per buffer zone area were taken and combined to form 4–5 bulked samples per buffer zone (Papers III and IV). At the first sampling occasion, soil samples were taken from the top 30 cm soil layer. The peat samples were further divided into surface peat (0–15 cm) and subsurface peat (15–30 cm). At the Asusuo buffer zone area, the peat and mineral soil layers were studied separately.

The effect of P loading on the P retention properties in the peat was studied using peat samples from Asusuo, Kirvessuo, Murtsuo and Kallioneva peatland buffer zone areas which were taken before the $\text{PO}_4\text{-P}$ adding experiment in 2001, and 5–8 days after the P adding experiment had ended in 2003 (Paper III).

2.2. Laboratory analyses

P desorption-sorption isotherms were determined according to the procedure described by Heikkinen et al. (1995). The added concentrations of $\text{PO}_4\text{-P}$ solution for podzolic E and C horizons were 0, 0.5, 1.0, 2.5, 5.0 and 10.0 mg P l^{-1} and to B horizons 0, 1.0, 2.0, 5.0 and 10.0 mg P l^{-1} . Corresponding concentrations added to the humus layer in the clear-cut areas and the adjoining unharvested buffer zones and to the peat in buffer zone areas was 0.0, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10 mg l^{-1} of P. Moist soil and P solution were added to bottles (dry soil to solution ration 1:40) and shaken on a reciprocating shaker at 180 rpm for one hour and then left to equilibrate for 23 hours, after which the suspensions were shaken again for 5 min at 120 rpm. The suspensions were filtered with glass fibre filters and a 0.2 μm membrane filter. The concentration of $\text{PO}_4\text{-P}$ remaining in the filtrate was determined using the molybdenum blue method.

For physical and chemical description of the studied soils, soil properties were determined from the Podzol horizons, the humus layers sampled in 1997 and 1998, and from peat sampled in 2001 from the buffer zone areas. All samples were analyzed for bulk density (BD), oxalate extractable iron (Fe_{ox}) and aluminum (Al_{ox}) and total carbon (C_{tot}). In addition, mineral soil horizons of Podzol profiles were analyzed for the proportion of particles <0.06 mm and humus layer and peat for cation exchange capacity (CEC), total nitrogen (N_{tot}) and pH.

Oven-dried (105 °C) samples were used for determining the soil properties. To determine Fe_{ox} and Al_{ox} , the soil samples were shaken in the dark with an acid (pH 3.0) ammonium oxalate buffer solution (0.2 M, 1/25 dry weight per volume) for 4 h and filtered with paper filters (Wang 1981). Fe_{ox} and Al_{ox} were measured using ICP-MS. C_{tot} and N_{tot} were measured with the combustion method (Leco CNS 1000). CEC was measured by extracting 1 g (dry weight) of soil with 50 ml of 0.1 M BaCl_2 solution. The bottles were shaken on a reciprocating shaker at 130 rpm for an hour and the suspensions were filtered with 0.2 μm membrane filter and exchangeable cations in the filtrate were analyzed. Soil pH was measured from an aliquot of the BaCl_2 extraction solution. Particles <0.06 mm were measured with the laser diffraction method (Coulter LS 230).

The water samples taken from the inflow, outflow and surface waters of the peatland buffer zone areas were filtered through 0.46 μm membrane filters. The filtrates were analysed for $\text{PO}_4\text{-P}$ with the molybdenum blue method.

The ^{32}P bound in the different soil layers was extracted with 0.2 M acid (pH 3) ammonium oxalate (Wang, 1981) and the ^{32}P assimilated in the vascular plant and moss samples was

measured by combusting the samples and dissolving the ashes in HCl (Paper IV). ^{32}P activity in oxalate and HCl solution was measured using liquid scintillation counting.

2.3. Calculations and statistical analyses

For conventional desorption-sorption isotherms, the amount of sorbed P (mg g^{-1}) was calculated as a function of P concentration in equilibrium solution (mg l^{-1}). A modified Langmuir equation (1) was fitted to the empirical data (Hartikainen and Simojoki 1997).

$$q = \frac{P_{\max} Kc}{1 + Kc} - q_0 \quad (1)$$

q = P sorbed
 P_{\max} = maximum P sorption
 K = constant
 c = P in equilibrium solution
 q_0 = instantly labile P

The intersection point on the concentration axis, i.e. the equilibrium phosphorus concentration (EPC_0) where no net desorption or sorption occurs, was graphically determined. EPC_0 gives an estimate of the threshold concentration of soil solution P above which net reduction in P concentration occurs.

To achieve initial mass isotherms, sorbed or desorbed P (mg g^{-1}) was calculated as a function of added P (mg g^{-1}) and a linear equation was fitted to the data (2) (Nodvin et al. 1986, Giesler et al. 2002). Addition levels corresponding to 0–5 mg l^{-1} were used because within that range the relation between added and sorbed or desorbed P for most soils was linear.

$$P_s = \alpha * P_a - \beta \quad (2)$$

P_s = P sorbed
 P_a = P added
 α, β = constants

Two measurements along with EPC_0 were used to describe soil P retention properties: P_0 which is the desorbed amount of P (mg g^{-1}) at the adding level 0 mg P l^{-1} and indicates instantly labile P in soil, and P_{10} which is P sorbed (mg g^{-1}) at the adding level 10 mg P l^{-1} and describes measured maximum sorption. In addition, parameter values of P_{\max} from the Langmuir fit and α from the initial mass isotherm were also used as reference values. P_{\max} describes maximum sorption and α sorption efficiency. The value of α varies from 0 to 1 where 0 indicates no sorption and 1 complete sorption of added P.

The P sorbed is presented as gravimetric concentrations (mg g^{-1}) to make the results more comparable with those from earlier studies. Thus, no allowance is made for the widely differing bulk densities of the organic soils and the mineral soils (see Table 3). It should therefore be noted that there may be differences in actual P retention capacity (in g per soil volume)

between soils even if the gravimetric (g per soil mass) retention capacities do not indicate any difference.

The reference values were used to test the differences in P retention properties between mineral soil horizons, humus layer and peat. Data from the first sampling occasion for the humus layer and peat was used for the analysis. One-way ANOVA was used to test the differences between the soil categories and Tukey's post-hoc test for pairwise comparisons.

Non-parametric Spearman correlation analysis was used to test correlation within the reference values, and correlations between reference values and Fe_{ox} and Al_{ox} .

The reference values EPC_0 , P_0 and P_{10} were used to test the differences between sampling times before and after P loading. The difference between sampling times for the humus layer was tested with repeated measures ANOVA using sample location (clear cut or buffer zone) as the grouping factor and sampling time as the repeated or within factor (Paper II). In the peatland buffer zone areas the differences in soil P retention properties before and after the P adding experiment were tested with Wilcoxon signed rank test (Paper III).

The outflow of the added P from buffer zones (P_{out} , kg) was calculated as:

$$P_{out} = \sum_{i=0}^t \frac{(OP_t - BP)}{10^6} * q_t \quad (3)$$

OP_t = PO_4 -P (mg l⁻¹) in outflow

BP = Background PO_4 -P concentration (mg l⁻¹) in outflow

q_t = Runoff (l) at day t .

t = Day following P addition

Interpolated values for outflow PO_4 -P concentration and runoff were calculated for days where data was missing. If the difference OP_t - BP was negative, the outflow of the added P was set as 0. The total retention of P by buffer zones was then calculated as the difference between the added 10 kg of PO_4 -P and the total P outflow (P_{out}) (Paper III).

Estimation of the retention of P by soil and vegetation was based on the recovery of added ³²P (Paper IV). Differences in specific activities of ³²P between vascular plants, mosses and soil samples were tested using one-way ANOVA and Tukey's post-hoc test for pairwise comparisons.

3. RESULTS

3.1. Soil properties at the study sites (I, II, III)

The studied Podzol profile at Haukkakangas showed typical features for podzolic soil, i.e. enrichment of Al_{ox} , Fe_{ox} and C_{tot} in the B horizon and depletion of Al_{ox} and Fe_{ox} in the E horizon (Table 3, Paper I). The physical and chemical properties of the mineral soil horizons E, B and C were similar to previously studied Podzol horizons in Nordic countries (Kubin 1983, Tamminen and Starr 1990, Westman 1990, Melkerud et al. 2000, Mokma et al. 2004).

In the humus layer, the bulk density was lower and the content of Al_{ox} , Fe_{ox} and N_{tot} was higher in the buffer zones than in the clear-cut areas (Table 3). Bulk densities, C_{tot} , and CEC

Table 3. Soils studied for their P retention properties were described with bulk density (BD), oxalate extractable Al (Al_{ox}) and Fe (Fe_{ox}), cation exchange capacity (CEC), total organic carbon (C_{tot}) and nitrogen (N_{tot}), pH of the CEC solution and the proportion of particles <0.06 mm. Figures are mean values \pm SD except for humus layer in buffer zones at C1 and C3 where the number of samples was one. Soil data has not been measured from Vanneskorvenoja buffer zone area. - Not measured.

		BD g cm ⁻³	Al_{ox} g kg ⁻¹	Fe_{ox} g kg ⁻¹	CEC mmol kg ⁻¹	C_{tot} %	N_{tot} %	pH	<0.06 mm %	n
<i>Podzolic upland soil</i>										
Haukkakangas	O horizon	0.12 \pm 0.02	1.0 \pm 0.4	1.1 \pm 0.5	-	47 \pm 5	-	-	-	6
	E horizon	0.96 \pm 0.21	0.3 \pm 0.1	0.1 \pm 0.1	-	1.0 \pm 0.3	-	-	18 \pm 2	3
	B horizon	1.36 \pm 0.06	20.2 \pm 10.0	6.0 \pm 1.6	-	1.1 \pm 0.7	-	-	15 \pm 2	3
	C horizon	1.48 \pm 0.06	2.3 \pm 0.8	1.0 \pm 0.6	-	0.1 \pm 0.0	-	-	27 \pm 45	3
<i>Humus layer in clear-cut areas and adjoining unharvested buffer zones</i>										
C1	Buffer zone	0.06	3.5	5.2	249	34	1.7	3.2	-	1
	Clear-cut	0.15 \pm 0.02	1.4 \pm 0.3	1.9 \pm 0.0	273 \pm 57	32 \pm 5	1.4 \pm 0.1	3.3 \pm 0.2	-	2
	Buffer zone	0.07 \pm 0.01	4.9 \pm 0.2	7.9 \pm 1.1	321 \pm 65	43 \pm 6	2.0 \pm 1.0	3.2 \pm 0.1	-	2
	Clear-cut	0.11 \pm 0.00	1.2 \pm 0.5	1.5 \pm 1.3	240 \pm 25	41 \pm 10	1.3 \pm 0.3	3.0 \pm 0.2	-	4
C3	Buffer zone	0.05	1.1	2.7	356	49	2.0	3.1	-	1
	Clear-cut	0.10 \pm 0.01	0.8 \pm 0.2	0.9 \pm 0.0	285 \pm 22	41 \pm 2	1.3 \pm 0.1	3.3 \pm 0.1	-	2
<i>Peat soil in peatland buffer zone areas</i>										
Asusuo	0–15 cm	0.16 \pm 0.12	3.2 \pm 0.6	3.5 \pm 1.5	155 \pm 52	20 \pm 7	0.9 \pm 0.3	4.1 \pm 0.1	-	9
	15–30 cm	0.15 \pm 0.08	2.9 \pm 0.2	4.1 \pm 1.5	210 \pm 43	36 \pm 4	1.7 \pm 0.2	4.4 \pm 0.2	-	8
Kivressuo	Mineral soil	1.05 \pm 0.02	1.6 \pm 0.2	0.9 \pm 0.2	27 \pm 12	2 \pm 1	0.1 \pm 0.0	4.3 \pm 0.1	-	9
	0–15 cm	0.14 \pm 0.03	1.3 \pm 0.2	8.7 \pm 0.6	422 \pm 46	48 \pm 2	1.8 \pm 0.0	4.0 \pm 0.1	-	4
Murtsuo	15–30 cm	0.17 \pm 0.05	2.2 \pm 1.3	3.2 \pm 1.2	272 \pm 42	50 \pm 4	1.6 \pm 0.2	3.5 \pm 0.2	-	4
	0–15 cm	0.19 \pm 0.06	4.0 \pm 0.7	3.2 \pm 0.5	390 \pm 69	34 \pm 9	1.7 \pm 0.4	4.3 \pm 0.2	-	4
Kallioneva	15–30 cm	0.15 \pm 0.02	6.1 \pm 0.3	2.6 \pm 0.4	332 \pm 23	46 \pm 2	2.1 \pm 0.1	3.9 \pm 0.1	-	4
	0–15 cm	0.05 \pm 0.02	2.6 \pm 0.3	4.3 \pm 1.1	247 \pm 68	36 \pm 10	1.1 \pm 0.2	4.0 \pm 0.2	-	4
Hirsikankaansuo	15–30 cm	0.06 \pm 0.10	2.5 \pm 0.5	3.2 \pm 0.9	277 \pm 47	45 \pm 2	1.5 \pm 0.3	3.8 \pm 0.2	-	4
	0–15 cm	0.08 \pm 0.02	2.2 \pm 0.1	7.5 \pm 1.4	202 \pm 23	40 \pm 7	1.7 \pm 0.6	4.0 \pm 0.1	-	4
	15–30 cm	0.08 \pm 0.01	1.5 \pm 0.4	2.7 \pm 0.1	124 \pm 23	51 \pm 2	2.6 \pm 0.3	3.5 \pm 0.1	-	4

were within the variation presented in previous studies for humus layers (Tamminen and Starr 1990, Westman 1990).

At the peatland buffer zone areas surface layer peat had higher Fe_{ox} than subsurface peat. Peat bulk densities were slightly higher than in previous studies except for Kallioneva and Hirsikankaansuo (Päivänen 1973, Westman 1981). Al_{ox} and Fe_{ox} content in peat (Table 3) were approximately at the same order of magnitude as total Al and Fe determined in peat (Nieminen 2003, 2004). CEC and N_{tot} were similar to previously presented results (Westman 1981, Nieminen 2003, 2004) even though higher N_{tot} concentrations have been determined from drained peatlands (Nieminen and Penttilä 2004).

The Podzol B horizon had the highest Al_{ox} and Fe_{ox} compared to the E and C horizons and to the peat and the humus layer. In E and C horizons Al_{ox} and Fe_{ox} concentration in g kg^{-1} were even lower than in the peat and humus layer (Table 3), but when the different bulk densities were taken into account, the amount per volume basis was much higher for mineral soil horizons than for the peat soils or for the humus layer. When the peat and the humus layer were compared, peat contained more Al_{ox} and Fe_{ox} .

3.2. P sorption properties of Finnish forest soils (I, II, III)

According to the isotherms, the B horizon showed the highest P sorption efficiency of all the studied soil layers (Fig. 6). In this horizon, the release of instantly labile P (P_0) and the threshold concentration for net sorption (EPC_0) were lowest and measured maximum sorption (P_{10}) and sorption efficiency (α) were highest (Table 4). Lowest P sorption was in the humus layer in clear-cut areas where the release of labile P and the threshold concentration for net sorption was high and maximum sorption low. There was high variation in the P sorption properties of the peat soil but generally the desorption-sorption behaviour was similar to the humus layer in buffer zones, i.e. lower than in the B horizon but higher than in humus layer in clear-cut area.

Measured maximum sorption (P_{10}) for humus layer in buffer zones and in peat was higher than in the C horizon in the mineral soil, when retention was measured per soil mass unit (Fig. 6). Taking into account the different bulk densities of the peat soil and the mineral soil, the sorption per soil volume unit would be much higher for mineral soil than for peat (Paper IV Fig. 3).

The measured maximum sorption and sorption efficiency (α) was higher in surface peat layer (0–15 cm) than in subsurface peat (15–30 cm) (Table 4). Correspondingly, humus layer in the buffer zones retained P more efficiently than the humus layer in clear-cut areas (Fig. 6, Paper II Figs. 2 and 3). There were no significant differences in P_{max} values between the soil categories.

There was high correlation between the instantly labile P (P_0) and the threshold concentration for net sorption (EPC_0), and between the measured maximum sorption (P_{10}) and the sorption efficiency (α) (Table 5). The soil Al_{ox} and Fe_{ox} correlated with the measured maximum sorption and sorption efficiency (α), and the highest correlations were achieved when the sum of $\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}}$ was used (Table 5, Fig. 7).

P retention in the humus layer in the buffer zones and in the clear-cut area had decreased between the first and the second sampling occasion (Paper II Figs. 2–3) which was shown as increase in instantly labile P (P_0) and decrease in measured maximum sorption (P_{10}) (Table 4). In peatland buffer zone areas, P addition in 2003 decreased the measured maximum sorption and sorption efficiency in the peat in all the areas (Table 4, Paper III Figs. 9–12). In Asusuo and Murtsuo, also instantly labile P and threshold concentration for net sorption had increased.

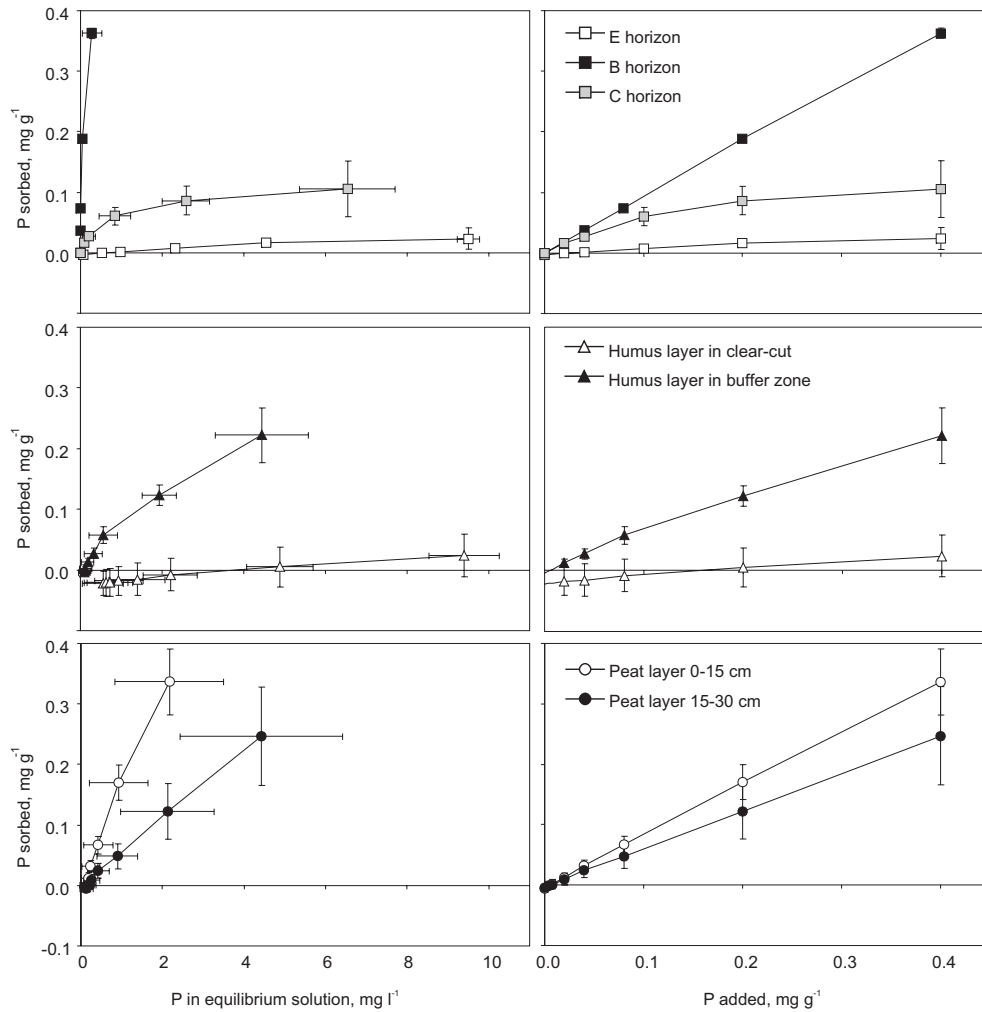


Figure 6. Phosphorus sorption in the mineral soil horizons of Podzol profile (E, B and C in graphs in the top row), humus layer in clear-cut area and adjoining unharvested buffer zone (graphs in the middle row) and in peat layers 0–15 cm and 15–30 cm (graphs in the bottom row). In isotherms on the left, P sorbed or desorbed is presented as the function of P in equilibrium solution when P added ranged from 0 to 10 mg l^{-1} . On the right, initial mass isotherms demonstrate sorption or desorption as the function of added P between 0–0.4 mg g^{-1} (corresponding to the added concentrations of 0–5 mg l^{-1}). Samples from first sampling occasion of humus layer and peat were used. In isotherms, average values \pm SD are presented.

Table 4. Reference values describing P retention properties of upland soil with podzolic horizons, humus layer in clear-cut areas and adjoining unharvested buffer zones and peat in peatland buffer zone areas. Median (Md), high and low quartiles (Q_{25} and Q_{75}), minimum (Min) and maximum (Max) values are given. P_0 is instantly labile P, P_{10} is measured maximum sorption, EPC_0 is the threshold concentration above which sorption occurs, α is the slope of the initial mass isotherm and describes sorption efficiency and P_{max} sorption maximum defined with Langmuir equation. For humus layer in clear-cut areas, humus layer in buffer zones and peat 0–15 cm, 1st sampling represents conditions before and 2nd sampling after soil had exposed to elevated PO_4 -P load.

	Podzol			Humus layer				Peat			
	E horizon	B horizon	C horizon	Clear-cut		Buffer zone		0–15 cm	15–30 cm		
				1 st sampling	2 nd sampling	1 st sampling	2 nd sampling	1 st sampling	2 nd sampling		
P_o , $\mu\text{g g}^{-1}$	Md	2.07	0.06	0.00	17.2	113.7	1.58	71.4	4.04	6.48	2.48
	Q ₂₅	1.92	0.02	0.00	1.74	95.1	0.45	29.0	1.56	1.84	1.80
	Q ₇₅	3.19	0.13	0.05	36.8	186.6	4.91	168.6	6.40	11.0	4.54
	Min	1.76	0.00	0.00	0.56	84.1	0.36	5.39	0.08	0.78	0.09
	Max	4.30	0.22	0.10	56.0	327.6	11.60	248.2	26.3	101.6	18.9
P_{10} , mg g^{-1}	Md	0.03	0.36	0.08	0.02	−0.06	0.22	0.02	0.32	0.23	0.25
	Q ₂₅	0.02	0.36	0.08	0.00	−0.15	0.19	−0.06	0.29	0.21	0.22
	Q ₇₅	0.03	0.37	0.12	0.06	−0.03	0.25	0.09	0.38	0.30	0.31
	Min	0.00	0.35	0.08	0.00	−0.26	0.17	−0.15	0.23	0.12	0.08
	Max	0.04	0.37	0.16	0.08	0.01	0.28	0.17	0.43	0.38	0.38
EPC_o , mg l^{-1}	Md	0.77	0.01	0.00	3.50	18.7	0.06	7.75	0.12	0.20	0.08
	Q ₂₅	0.58	0.00	0.00	0.06	14.9	0.01	3.58	0.04	0.05	0.05
	Q ₇₅	0.86	0.01	0.00	10.0	43.9	0.16	14.4	0.21	0.14	0.14
	Min	0.40	0.00	0.00	0.02	9.25	0.01	0.16	0.00	0.02	0.00
	Max	0.96	0.01	0.01	35.0	48.1	0.36	26.7	0.86	17.9	2.13
α	Md	0.10	1.00	0.39	0.13	0.16	0.64	0.32	0.83	0.66	0.66
	Q ₂₅	0.08	0.99	0.39	0.06	0.15	0.60	0.25	0.73	0.59	0.51
	Q ₇₅	0.11	1.00	0.50	0.23	0.17	0.67	0.37	0.93	0.78	0.75
	Min	0.06	0.96	0.38	0.04	0.13	0.50	0.06	0.60	0.38	0.22
	Max	0.13	1.00	0.60	0.24	0.24	0.76	0.42	1.00	0.96	0.97
P_{max}	Md	1.03	1.39	0.38	0.10	5.98	0.57	8.05	0.73	0.60	0.80
	Q ₂₅	0.60	1.22	0.33	0.08	5.98	0.30	5.98	0.62	0.45	0.60
	Q ₇₅	24.0	1.64	0.42	0.25	5.98	0.88	20.7	0.85	1.33	1.70
	Min	0.18	1.07	0.28	0.04	5.98	0.17	0.83	0.50	0.32	0.38
	Max	47.0	2.01	0.46	3.27	10.1	1.14	66.5	162.6	8.17	69.1
n	3	6	3	11	9	4	12	25	17	24	

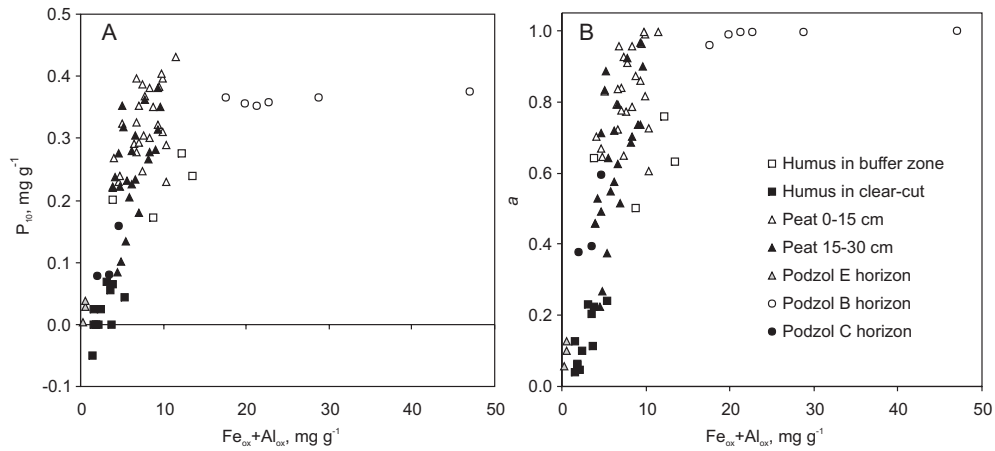


Figure 7. Scatter plots showing the relation between oxalate extractable iron and aluminium in soil ($\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}}$) and reference values P_{10} (A) and α (B).

Table 5. Correlation between reference values used to describe P retention properties and soil Fe_{ox} and Al_{ox} . The significance of the correlation is expressed with asterisks (* $p < 0.05$, ** $p < 0.005$, *** $p < 0.001$).

	P_0	P_{10}	EPC_0	α	P_{max}	Fe_{ox}	Al_{ox}
P_{10}	-0.313**						
EPC_0	0.948***	-0.446***					
α	-0.314**	0.980***	-0.451***				
P_{max}	0.026	0.182	0.047	0.135			
Fe_{ox}	-0.077	0.745***	-0.207	0.727***	0.124		
Al_{ox}	-0.222*	0.656***	-0.287*	0.679***	0.101	0.492***	
$\text{Fe}_{\text{ox}} + \text{Al}_{\text{ox}}$	-0.165	0.812***	-0.274	0.817***	0.181	0.907***	0.750***

3.3. Total P retention by the peatland buffer zone areas (III, IV)

Before starting the $\text{PO}_4\text{-P}$ adding period the background $\text{PO}_4\text{-P}$ concentrations in the inflow and outflow waters were approximately 0.010 mg l^{-1} at all six buffer zone areas. $\text{PO}_4\text{-P}$ additions increased the inflow $\text{PO}_4\text{-P}$ concentrations to significantly higher level than the background at all buffer zone areas, especially at Kallioneva, where the water flow from the adding point to the buffer zone area was very slow (Figs. 8 and 9). The outflow of P increased at Asusuo, Kirvessuo, Murtsuo and also at Hirsikankaansuo, but only during the second adding period. At Kallioneva and Vannesorvenoja and also at Hirsikankaansuo, the outflow $\text{PO}_4\text{-P}$ concentrations remained at the background level throughout the first adding period. After the adding had ended the outflow concentrations of $\text{PO}_4\text{-P}$ from Asusuo exceeded the background concentrations until the autumn of 2004, and from Kirvessuo and Murtsuo, until the autumn of 2003 (Fig. 8). The outflow concentrations of $\text{PO}_4\text{-P}$ from Kallioneva and Vannesorvenoja remained at the background level throughout the study period. The inflow concentrations at Kallioneva buffer zone were very high after the adding had ended. The inflow ditch formed a water basin where the added $\text{PO}_4\text{-P}$ remained when the runoff load water flow was low and slowly discharged to the buffer zone area along with increased runoff load by the end of the year.

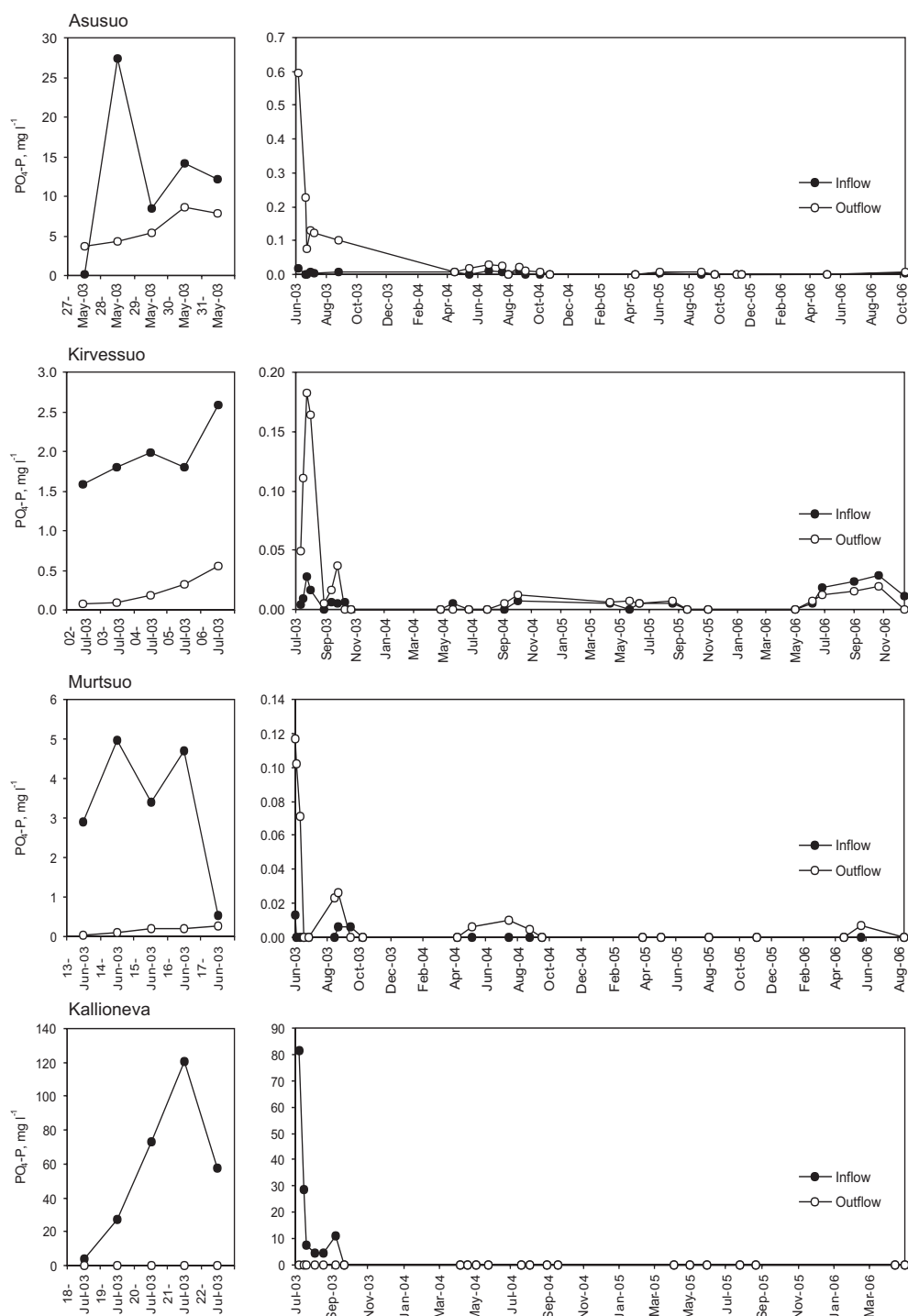


Figure 8. $PO_4\text{-P}$ inflow and outflow during the adding period in 2003 (left) and after the adding period in 2003-2006 (right) at Asusuo, Kirvessuo, Murtsuo and Kallioneva buffer zone areas.

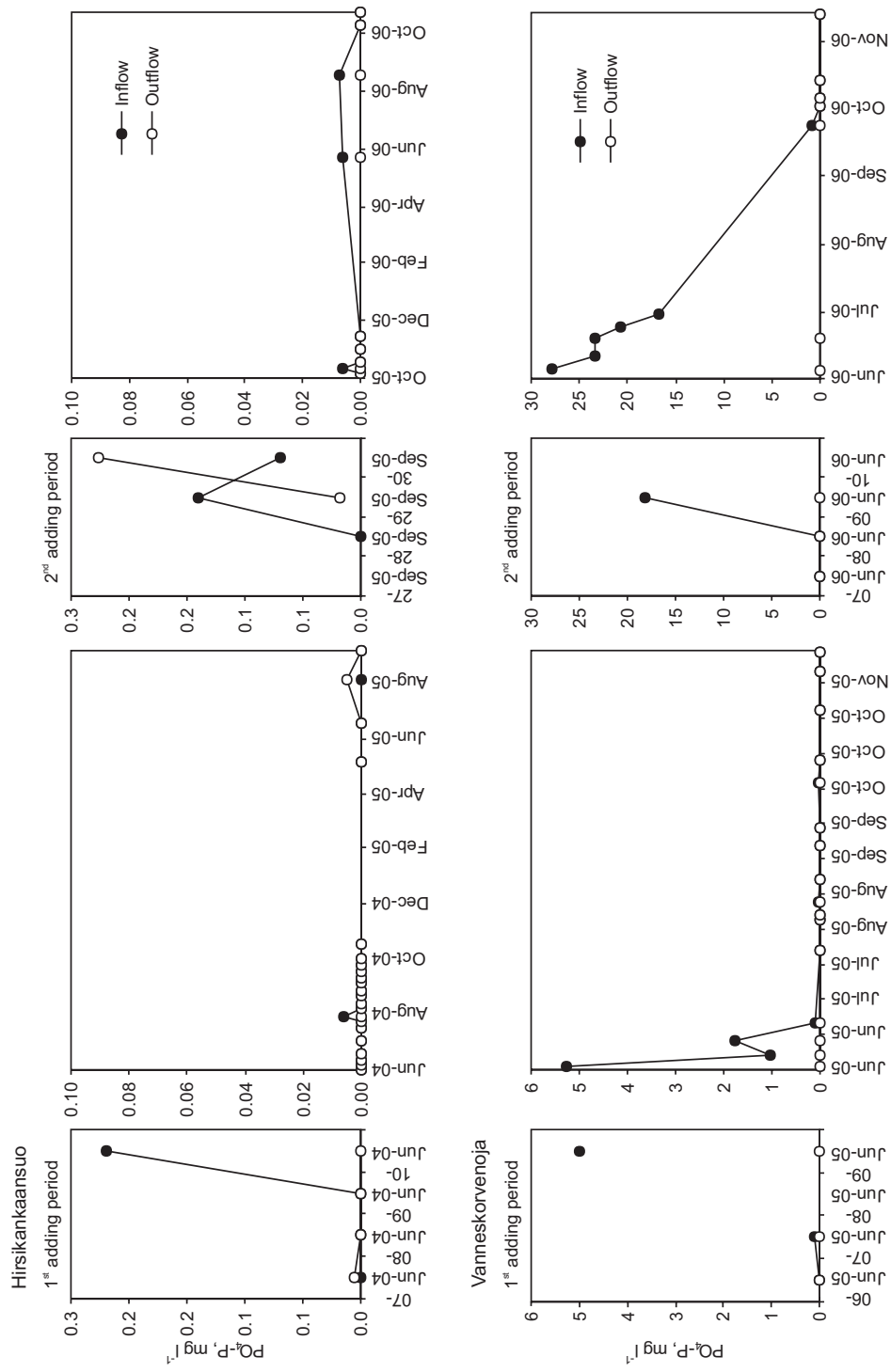


Figure 9. PO₄-P inflow and outflow during and after the first and second adding period at Hirsikankaansuo and Vanneskorvenoja buffer zone areas.

The average runoff load during the $\text{PO}_4\text{-P}$ solution adding periods to the six peatland buffer zone areas varied from 2 mm d^{-1} to 104 mm d^{-1} (Paper III). Kallioneva received the lowest and Asusuo the highest runoff load. Calculation based on the outflow concentration and runoff load indicated that the P retention at the end of the five-day adding period varied from 5.6 to 10 kg being the lowest at Asusuo and highest at Kallioneva and Vannesorvenoja buffer zone areas (Paper III). From Asusuo, Kirvessuo, Murtsuo and Hirsikankaansuo, outflow of added P continued after the adding period (Fig. 8 and 9). When this outflow was taken into the calculations (Paper III), total retention at the end of the follow-up period was 2.4, 9.5, 9.5 and 9.4 kg for the areas, respectively. The percentage of the added P retained by the buffer zone areas was thus 24%, 95%, 95% and 94% for Asusuo, Kirvessuo, Murtsuo and Hirsikankaansuo, respectively. The retention percentage for Kallioneva and Vannesorvenoja was 100%.

In Asusuo, P retention was also estimated as the recovery of ^{32}P in the soil and vegetation five days after the adding had ended, i.e. ten days after the start of the experiment (Paper IV). At that time, the recovery of ^{32}P was $28.9 \pm 5.6 \text{ MBq}$, thus, 16% of the added ^{32}P had been retained by the soil and vegetation at the Asusuo buffer zone (Table 6).

3.4. Allocation of the retained P (IV)

Higher specific activities of ^{32}P were found in the vegetation than in the soil, but there were no differences between vascular plants and mosses (Table 6, Paper IV). The surface peat had higher specific activity than the mineral soil layer but the subsurface peat showed no ^{32}P activity. 90% of the recovered ^{32}P (in MBq) was in soil, 3% in vascular plants and 5% in mosses (Table 6).

Table 6. Specific activities and recovery of ^{32}P in soil and vegetation in the Asusuo buffer zone. Percentages express recovery in relation to the total amount of added ^{32}P (185 MBq).

		Specific activity Bq g^{-1}	Recovery MBq	Recovery %
Soil	Surface peat	3.02 ± 0.73	22.6 ± 5.5	12.2 ± 3.0
	Mineral soil	0.20 ± 0.07	4.0 ± 1.2	2.2 ± 0.6
	Subsurface peat	0.00 ± 0.00	0.0 ± 0.0	0.0 ± 0.0
	Total	0.85 ± 0.18	26.6 ± 5.6	14.4 ± 3.0
Vegetation	Vascular plants	24.86 ± 5.17	0.9 ± 0.2	0.5 ± 0.1
	Mosses	13.12 ± 3.18	1.4 ± 0.3	0.7 ± 0.2
	Total	16.12 ± 2.71	2.3 ± 0.4	1.2 ± 0.2
Total recovery			28.9 ± 5.6	15.6 ± 3.0

4. DISCUSSION

4.1. Characterization of soil P sorption

Sorption-desorption isotherms visualize soil P retention characteristics but for quantitative analysis this visual information needs to be transformed into a numerical form. This quantification is specifically important when the connection between soil P retention capacity and soil chemical properties, such as Al and Fe content, is established. Numerical data is also needed for predicting the fate of increased P input in soil. Several approaches have been proposed for this quantification and here the applicability of different sorption equations and reference values are discussed.

The Langmuir equation has widely been applied to describe P retention in soil, probably because the parameter P_{max} represents a theoretical P sorption maximum in a soil. In Podzol B and C horizons the values of P_{max} i.e. the sorption maximum were approximately the same as the retention capacity determined at the highest addition level of 100 mg l⁻¹ for B and 50 mg l⁻¹ for C (Paper I: Fig. 1). In the E horizon, the humus layer and the peat there was large variation in the values of P_{max} and the fitting of the Langmuir equation gave the highest values for soils for which the visual interpretation of the isotherms indicated the lowest sorption capacity. In the B and the C horizons the measured sorption appeared to approach the saturation level whereas in the E horizon and the organic soil layers the sorption typically increased linearly without any saturation tendency. This lack of saturation is probably why the Langmuir equation failed to give reliable estimates for maximum sorption in the E horizon and the organic soil layers. Therefore, the parameter value P_{max} of the Langmuir equation may be a reliable estimate of maximal P retention only for the B and C horizons of the mineral soils. However, it should also be noted that maximum sorption is generally achieved with bathing solution (i.e. adding solution) concentrations much higher than those found in soil solutions under normal conditions in nature. This, as well as the fact that the sorption maximum is determined in laboratory conditions, where the soil-solution contact is optimized, indicated that P_{max} overestimate the sorption in field conditions (e.g. Richardson 1985, Heikkinen et al. 1995), and thus reduce its applicability in ecological studies.

Isotherms, where sorbed or desorbed P is presented as a function of P in equilibrium solution, describe the equilibrium state between P in soil and in soil solution, but they provide little information on the change in P retention against an increase in added P. This change can be estimated by plotting P sorption as a function of both P concentration in equilibrium solution and P in bathing solution in the same graph (Hartikainen 1982). A simpler way to study this change is to directly plot the sorbed P (in mg g⁻¹) as the function of the added P (in mg g⁻¹). A linear equation is then fitted to the data to achieve the initial mass isotherm (Nodvin et al. 1986). The values for the parameter α , which is the slope of the isotherm, vary from 0 to 1, where 0 indicates no retention and 1 complete retention of P (Nodvin et al. 1986, Giesler et al. 2002). In our data, α correlated positively with Al_{ox} and Fe_{ox} in the soil except for the B horizon, where all values for α were close to 1 indicating complete P retention. There appeared to be a threshold concentration of Al_{ox} and Fe_{ox} in the soil above which P retention was complete. With this data, this threshold value for the sum of Al_{ox} and Fe_{ox} in soil was approximately 11.5 mg g⁻¹ (Eq. 4). Below this threshold, α increased with the concentration of Al_{ox} + Fe_{ox} in the soil linearly ($r = 0.769$, $p < 0.001$) (Eq. 5).

$$\alpha = 1, \quad \text{when } \text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}} > 11.5 \text{ mg g}^{-1} \quad (4)$$

$$\alpha = 0.08 * (\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}}) + 0.13, \quad \text{when } \text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}} \leq 11.5 \text{ mg g}^{-1} \quad (5)$$

In the modified Langmuir isotherm desorption is described with the parameter q_0 . The mechanistic interpretation for q_0 is that it represents the pool of instantly labile P in the soil (Hartikainen and Simojoki 1997). The desorption of P at the addition level of 0 mg P l⁻¹ (P_0) can probably also be used as an estimate of the soil labile P pool because of high correlations with q_0 (Väänänen et al. 2004). Several factors in the extraction procedure of P_0 , such as soil-solution ratio, vigour of shaking, time and temperature used in extraction have an effect on the P extracted from soil at different addition levels (e.g. Barrow and Shaw 1979, Bramley et al. 1992, Peltovuori and Soinne 2005), but because these factors were kept constant, the values of P_0 could be used to compare desorption tendencies between the studied soils. The value of EPC_0 , i.e. the threshold concentration in soil solution above which net sorption of P occurs from soil solution in the soil matrix or from water in the bottom sediment (e.g. Taylor and Kunishi 1971, Koski-Vähälä and Hartikainen 2001, Koskiahho et al. 2003, McDowell and Sharpley 2003, Peltovuori 2006), was strongly related to the pool of instantly labile P in soil.

The single value P sorption index in soil developed by Bache and Williams (1971) has been applied in several studies as an estimate of soil maximum P adsorption capacity (e.g. Cuttle 1983, Richardson 1985, Nieminen and Jarva 1996). The index is calculated as the ratio of sorption at a given P addition level and the logarithm of the resulting equilibrium P concentration. However, an almost as good estimate for maximum P adsorption capacity as the index was achieved in the study by Bache and Williams (1971), when sorption at a single high addition level was used. The estimate of the maximum sorption used in the present study (P_{10}) had a high correlation with the slope α of the initial mass equation and they both correlated strongly with the Al_{ox} and Fe_{ox} content of soil.

Single value P sorption indices and reference values describe desorption or maximum sorption tendency of soils. The interpretation of soil sorption properties may differ depending on which reference values are used. For example, the values of P_{10} and α indicated higher P retention (in mg g⁻¹) for the peat than for the C horizon of the Podzol profile whereas the interpretation of P_0 and EPC_0 resulted in an opposite conclusion. Therefore, if reference values are used, a combination of two reference values is recommended, one relating to desorption (e.g. P_0 and EPC_0) and the other to chemical sorption capacity (P_{10} and α) for reliable interpretation of soil P retention properties.

The P retention in the humus layer noticeably decreased when the soil had been dried before analyzing and this change was shown as an increase in P_0 and EPC_0 and a decrease in P_{10} (Väänänen et al. 2006). Changes in P retention properties have also been observed in dried peat and mineral soil (e.g. Kaila 1962, Turner and Haygarth 2001, Venterink et al. 2002, Peltovuori 2007). These results indicate that drying may not be a suitable pre-treatment for a soil sample if the aim is to describe soil P retention in natural conditions.

After an increased P load as a result of timber harvesting and artificial P addition, the P sorption capacity of both humus and peat decreased (Papers II and III). This indicated that the measured P retention described a momentary state in the soil rather than a constant property. Further assessment is needed to evaluate at which extent this change can be predicted from soil properties.

4.2. Relation between soil P retention properties and the risk of P leaching

In the Podzol profile, P retention properties varied considerably between the soil horizons. The humus layer overlying the mineral soil had a low P retention potential especially in clear-cut areas and a further decrease occurred with time, which was shown as an increase in labile P and a decrease in maximum P sorption (Papers I and II). The main source of the increased soluble P in the soil was probably the decomposition of cutting residues (e.g. Stevens et al. 1995, Palviainen et al. 2004). The P released from cutting residues may have saturated the P sorption sites of the humus layer. Additional factors for the decrease in P sorption may have been the drying of the surface soil in clear-cut areas (Redding et al. 2003) as a result of increased surface soil temperatures (Kubin and Kemppainen 1991) and the competition for sorption sites between P and soluble organic compounds that have been released as a result of harvesting.

The P retention in the E horizon was low apparently because of weathering-induced depletion of Al and Fe in the horizon (Paper I). The low content of chemically sorptive components in the E horizon and the humus layer imply that biological processes control the P cycling in these surface soil layers (Wood et al. 1984). In contrast to the humus layer and the E horizon, the large pool of Al and Fe compounds indicated that chemical P sorption was the main P retention process in the B horizon. The ability of the B horizon to retain P was more than 100 times higher than the estimated P input in the soil after clear-cutting (Paper I). Therefore, if water percolates through the B horizon, the risk of harvesting-induced P leaching is low. The high pool of soluble P in the horizons overlying the B horizon suggest that there may be risk of P leaching if water discharges horizontally through these layers. However, such events may be unlikely. Catchment level studies indicate that P is tightly conserved within upland catchments with podzolized B horizons (Wood et al. 1984, Stevens et al. 1995, Mattsson et al. 2003, Neal et al. 2003). There are several reasons which can explain this dominance of the B horizon in the P retention of the catchments with podzolic soils. The humus layer and the E horizon are typically shallower and have lower bulk density than the B horizon and therefore the mass and volume of the B horizon is larger. In addition, the soil surfaces are disturbed by harvesting and wood transporting machinery and especially in soil preparation for planting or seeding, and thus large areas of the B horizon are exposed and are then in a direct contact with the P released from cutting residues. However, accumulation of litter over the revealed B horizon may gradually start to change its P sorption properties towards those of the low-sorbing E horizon (Paper I).

The P retention in the humus layer was higher in the unharvested buffer strips than in the adjoining clear-cut areas (Paper II). This difference may be because of the higher Al_{ox} and Fe_{ox} content in the buffer zones. Accumulation of Al and Fe has been shown to occur in river banks and groundwater discharge areas where surface flow and base flow are mixed (Norrström 1993, Pellerin et al. 2002). Similarly to clear-cut areas, 3–4 years after harvesting the P retention capacity of the humus layer in buffer zones had decreased, except for the buffer zone at C3 (Paper II). The amount of P sorbed by the humus layer of the buffer zones at C1, C2 and C3 was estimated by assuming that the increase in P_0 describes sorption in the labile pool and decrease in P_{10} sorption in the permanent pool. Calculated for the total area of the buffer zones, the humus layer had retained 0.2–1.5 kg P at each buffer zone and 20% – 45% of it was in the labile pool. This calculation probably overestimated the actual retention because part of the sorption sites were probably occupied by organic compounds also and not only with PO_4 -P. Still, the retention by the buffer zones was low compared to the potential release of P after clear-cutting, approximately 3–6 kg of P per harvested hectare annually (Stevens et al. 1995,

Palviainen et al. 2004, Piirainen et al. 2004) and thus indicated that the significance of the humus layer in the buffer zones in retaining P against leaching is low.

A study on brook water quality by Haapanen et al. (2006) in the catchments C1, C2 and C3 showed that after clear-cutting the suspended P concentration had increased in all the studied catchments and soluble P concentration in catchments C1 and C2. In catchment C3, where the humus layer of the buffer zone had the highest P retention capacity (Paper I), no increase in the soluble P in brook water had occurred. Thus, although the P retention capacity of humus is generally low, some retention against leaching to a recipient brook may have occurred in the humus layer of the buffer zone of catchment C3. However, increased P leaching and loading from the catchments C1 and C2 indicates that the buffer zones in those areas may have been less efficient than the buffer zone in C3 and similar buffer zones in previous studies (Ahtiainen and Huttunen 1999).

The peat studied in the present paper was collected from peatland buffer zones which had been constructed on either pristine mires or restored and rewetted former drained peatland sites. There was large variation in the peat P retention properties in the data but it did not correlate with the initial state of the peatland, i.e. pristine or drained site (Paper III). The surface peat layer (0–15 cm) contained more Fe_{ox} and retained P more efficiently than the subsurface peat layer (15–30 cm). High variation in P retention properties seems to be typical for peatlands but higher P retention in the surface peat may not be generally applicable, as a more extensive data set indicated the opposite between-layer variation (Nieminen and Jarva 1996). However, higher P retention in the surface peat could be typical for peatland buffer zones as their P retention capacity is influenced by the sediment that is eroded from the catchment area upstream and deposited in the surface of the buffer zone. Further research is needed to clarify the influence of the deposited sediment on P retention by peatland buffer zones.

On average, the peatlands had a lower P retention potential and a higher desorption tendency than the podzolic upland soils (especially on the volumetric basis), and this may explain the results of the catchment-level studies, where the proportion of peatlands has been shown to be a good indicator of P in the runoff (Kortelainen and Saukkonen 1998, Kortelainen et al. 2006). After harvesting, P leaching typically increases at peatland-dominated catchments, and the risk of increased leaching is higher from nutrient poor sites than from more fertile site types (Knighton and Stiegler 1980, Ahtiainen and Huttunen 1999, Lundin 1999, Cummins and Farrell 2003, Nieminen 2003). This can be explained with the generally higher peat Al and Fe content on fertile, minerotrophic sites than on nutrient-poor ombrotrophic sites.

The peatland buffer zones efficiently retained the soluble P in the P addition experiment and, similarly to the humus layer, the sorption of added P by the peat was reflected as an increase in the labile P pool and a decrease in the maximum sorption (Paper III). If the P sorption in the soil of the buffer zones is calculated by assuming that the increase in P_0 describes sorption in the labile pool and the decrease in P_{10} sorption in the permanent pool, 56%, 25% and 17% of the P retained respectively by the Asusuo, Kirvessuo and Murtsuo buffer zones would have been in the soil. At Asusuo, the analysis of added ^{32}P indicated a significantly higher retention by the soil, i.e. 92% of the P retained by the buffer was in the soil (Paper IV). Although it may be difficult to assess the importance of soil P sorption capacity in overall P retention by buffer zones, the results from Asusuo indicated that sorption by soil is particularly important during high flow in early spring, when the vegetation has not yet developed (Paper IV).

The Kallioneva buffer zone area retained all the added P in the addition experiment (Paper III) but the peat P sorption capacity did not decrease as for the other buffer zones. The high P retention capacity of peat at Kallioneva may have buffered against any measurable changes in

P retention properties. Fractionation of the chemical P forms in the peat before and after the P addition might have revealed whether there were any changes in the sorbed P in Kallioneva.

The peat P retention properties determined in the laboratory did not correlate well with the field measurements of the total P retention by the buffer zone areas (Paper III). This indicated that other factors than peat P sorption capacity are involved in P retention. However, a high P retention capacity of the peat may have contributed to the sustainability of the retention. At the Kallioneva and Hirsikankaansuo buffer zone areas, where the peat had the highest P retention capacity, no P discharged from the areas after the adding had ended. In comparison, at the Asusuo, Kirvessuo and Murtsuo buffer zone areas with lower peat P retention capacities, P was released during the addition period and a few months after it. P sorbed by organic soils mostly remains in soluble form (Fox and Kamprath 1971, Rannikko and Hartikainen 1980) and the origin of the release was probably the labile P pool in peat from which P was slowly released.

4.3. Possibilities to remove soluble P from water flow by peatland buffer zone areas

Peatland buffer zones and other types of natural and constructed wetland buffer zone areas are applied to reduce nutrient and suspended solid loads from forested areas (e.g. Sallantausta et al. 1998, Kubin et al. 2000, Liljaniemi et al. 2003, Nieminen et al. 2005a, 2005b), from peat mining areas (Ihme 1994, Heikkinen et al. 1995) and from agricultural land (e.g. Uusi-Kämpä et al. 2000, Koskiahio et al. 2003). Internationally, wetland purification systems are also widely used to treat municipal waste waters. Despite the different origin of the anthropogenic diffuse load, or the initial state of the buffer zone area (pristine or restored wetland), there are similarities in the functioning efficiency and purification processes of wetland buffer zone areas. In general, wetland buffer zone areas are more efficient in reducing suspended solid loads than soluble nutrients, especially P (e.g. Ihme 1994, Koskiahio et al. 2003, Braskerud et al. 2005, Nieminen et al. 2005a, 2005b, Syversen 2005).

The size of the buffer, especially in relation to the catchment area has been regarded as one of the critical factors in the functioning of buffer zone areas used both in forestry and in agriculture (e.g. Uusi-Kämpä et al. 2000, Koskiahio et al. 2003, Braskerud et al. 2005, Nieminen et al. 2005a, Silvan et al. 2005). The advantage of a large size can be partly explained by the fact that potential P sinks in the buffer zone area are correspondingly larger, which results in a lower relative load and a lower probability of saturation of these sinks. In Paper III the total retention of the added P was highest at the largest buffer zones. However, small wetlands, too, may be useful in reducing nutrient loads (Braskerud 2002). The retention at the two significantly smaller areas was only slightly lower than that for the largest buffer zones, but one small area (Asusuo) retained significantly less P than all the other areas (24% vs. >95%) (Paper III). Previous studies indicate that beside the size of the buffer zone, hydraulic load and water residence time strongly affect the P retention efficiency (Ihme 1994, Koskiahio et al. 2003, Syversen 2005). Asusuo received a significantly higher hydrological load during the $\text{PO}_4\text{-P}$ adding period than the other areas. A high hydrological load generally leads to the formation of continuous flow channels across the buffer area. In such channels, the flow velocity is high and the water residence time low; both these factors are disadvantageous for an efficient retention of P. In Asusuo, the short water residence time was reflected in that elevated $\text{PO}_4\text{-P}$ concentrations at the outflow point were measured as early as two hours after the start of the P addition (Paper IV). In the areas with complete (100%) retention efficiency, the water residence time was probably long enough for all the P retaining chemical and biological processes to be efficiently involved.

Although the size of the buffer and the hydrological load are important in P retention, other factors may exist. The P addition experiment at Asusuo was conducted in spring when the vegetation had not yet fully developed, and as a result, the recovery of added P in the vegetation was low (Paper IV). During the growing period the vegetation has an important role in P retention by P accumulation in the living biomass (Richardson and Marshall 1986, Silvan et al. 2004b). In addition, the living vegetation slows down the water flow in the buffer zones and reduces the formation of preferential flow paths (Braskerud 2001). However, in the boreal region with a distinct winter period, the significance of the vegetation on P retention by buffer zone areas may be limited because a large part of the annual runoff occurs during the snow-melt period early in spring before the beginning of the growing season (Liljaniemi et al. 2003, Koskiahio et al. 2003). In addition, a significant part of the P retained by the biomass may be released when the annual parts of the vegetation are decomposed (Richardson and Marshall 1986, Silvan et al. 2004b, Uusi-Kämpä 2005). A long-term budget calculation by Huttunen et al. (1996) even indicated that the P stored by the vegetation of the buffer zone may decrease. Vegetation can form a permanent P sink only as long as its biomass increases and P is stored in perennial parts. Also the decomposition rate of P containing organic matter has to be slower compared to what is being produced.

The age of the buffer zone area can affect its P retention efficiency. Newly formed buffer zone areas can considerably increase the leaching of P (Sallantausta et al. 1998, Vasander et al. 2003). This leaching has been related to the increase in the soluble P pool as a result of rewetting of the soil (Knighton and Stiegler 1980, Venterink et al. 2002). Release of P from Fe-compounds due to anaerobic conditions may be the reason why the soluble P pool increases (Mahapatra and Patrick 1969). In addition, P release from a newly rewetted peatland buffer zone area may be related to changes in vegetation composition due to changing hydrological condition. At the Vanneskorvenoja buffer zone, the P outflow was high during about three years after its restoration (Vasander et al. 2003). During that time period, the changes in its vegetation cover (e.g. decrease in *Carex globularis* and increase in *Calamagrostis purpurea*, *Eriophorum vaginatum*, *Betula pubescens* and bryophyte) indicated that the vegetation was still adapting to new environmental conditions (Paper III). Similarly, Liljaniemi et al. (2003) reported increased P outflow from newly formed buffer zones where the vegetation cover was under development. However, because the Vanneskorvenoja buffer zone retained all of the added 10 kg of P in our P addition experiment carried out 7–8 years after restoration (Paper III) it appears that although a buffer zone would initially release P during and after construction, it will later function as a significant, sustainable P sink. Therefore, restoration of sections of drained peatlands can be recommended as an effective means to reduce water eutrophication in forested catchments, although their rewetting may initially cause some extra P outflow.

5. CONCLUSIONS

The sorption isotherms provide an extensive description of the P retention characteristics in soil but their construction is laborious. Single value sorption indices or reference values are simple to determine but one describing desorption tendency and one describing sorption are needed to adequately describe the soil characteristics. The combination of parameter α and P_0 may provide a suitable description of the P retention at the concentration range occurring in forest areas. Values for α can be predicted as a function of Al_{xo} and Fe_{ox} , which can be easily achieved by simple analytics and are even widely available in literature. The presence of in-

stantly labile P could not be predicted by the studied soil properties but the determination process of P_0 is fast, simple and affordable.

The P retention capacity of the B horizon of the Podzol profiles greatly exceeded the potential P release after forest clear-cutting and if the water from clear-cut area flows vertically through the B horizon, the leaching risk of soluble P is low. The humus layer and the E horizon apparently delay P leaching in a watercourse and their contribution to P retention is thus to prolong the time for biological P retention processes to take place. Therefore, establishing contact between the water flow, especially from managed forest areas, and the highly sorptive B horizon may help to prevent soluble P leaching from managed forest areas. In peatland buffer zone areas the P sorption in the peat contributed to the total P retention but other factors had a larger impact on the P retention efficiency by the buffer zone areas. However, a high P retention capacity in the peat may have contributed to the sustainability of their P retention and therefore, the peat P retention properties should be evaluated when selecting sites for buffer zone areas.

Even though the large buffer zone areas were the most efficient in retaining P, also small areas were useful in decreasing the P load to watercourses. Therefore, even small buffer zone areas should be formed for water protection purposes, because they are efficient in reducing P loads, and require no maintenance after construction. Factors contributing to an efficient P retention were large size of the buffer zone area and low hydrological loads whereas a large hydrological load combined with the formation of preferential flow paths, especially during early spring or late autumn was disadvantageous for an efficient P retention.

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